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Foam Prevention in Purge and Trap Analysis

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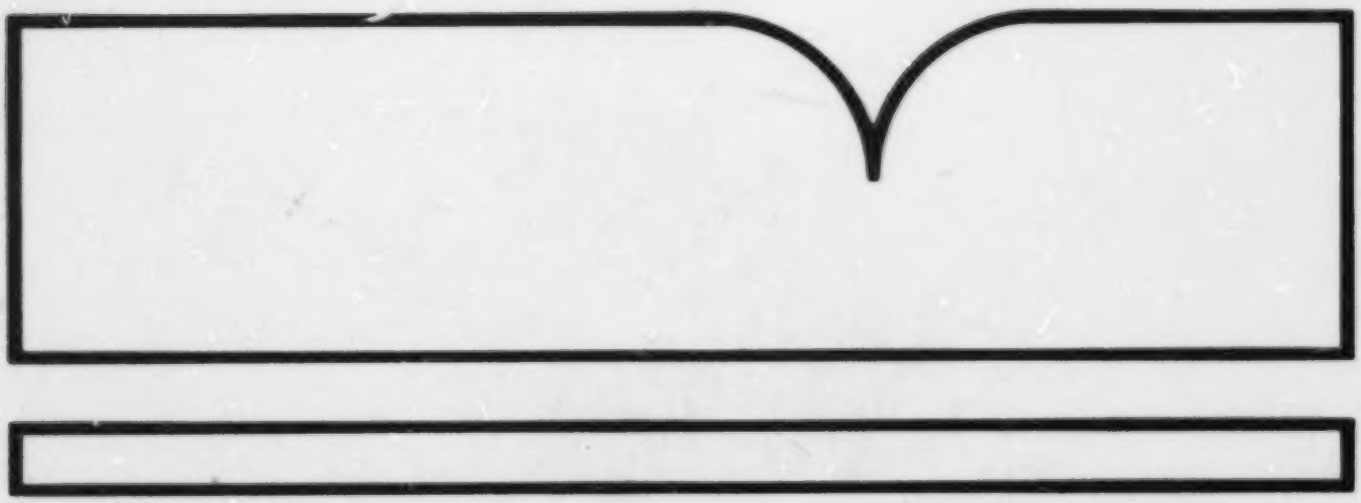

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16. ABSTRACT

Volatile organics are often separated from water samples by bubbling an inert gas through the water and collecting the organics on a sorbent trap, a technique known as purge and trap. Unfortunately, during the analysis of many water samples, foam can climb through the apparatus and contaminate the trap. This research project has investigated both chemical and mechanical antifoaming techniques. A total of 27 potential chemical antifoaming agents were evaluated for their ability to control foam. Two silicone-based commercial antifoam emulsions, Dow Corning Antifoam C and General Electric AF-72, were rated superior overall. The final protocol specifies use of 2 drops of purified silicone antifoam emulsion (General Electric AF-72) in a 5.0-mL sample which is purged in a 60-mL purge flask. The procedure was validated with seven volatile compounds (29-159 ng) spiked into four wastewaters. Mean recovery (vs. purge of distilled water) was 97%.

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Foam Prevention in Purge and Trap Analysis

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Volatile organics are often separated from water samples by bubbling an inert gas through the water and collecting the organics on a sorbent trap, a technique known as purge and trap. Unfortunately, during the analysis of many water samples, foam can climb through the apparatus and contaminate the trap. This research project has investigated both chemical and mechanical antifoaming techniques. A total of 27 potential chemical antifoaming agents were evaluated for their ability to control foam. Two silicone-based commercial antifoam emulsions, Dow Corning Antifoam C and General Electric AF-72, were rated superior overall. The final protocol specifies use of 2 drops of purified silicone antifoam emulsion (General Electric AF-72) in a 5.0-mL sample which is purged in a 60-mL purge flask. The procedure was validated with seven volatile compounds (29–159 ng) spiked into four wastewaters. Mean recovery (vs. purge of distilled water) was 97%.

Foams are agglomerations of gas bubbles separated from each other by thin liquid films (*1*). Surface-active solutes impart a surface elasticity to the liquid which allows formation of foam (*1–5*). The object of an antifoaming agent is to alter the surface characteristics of the liquid to disfavor foaming by decreasing surface viscosity and increasing rate of drainage. The chemical and physical properties desirable in an antifoaming agent include: (a) insolubility; (b) dispersion over the liquid surface; (c) inertness; and (d) nonvolatility. On the basis of reviews of chemical antifoams (*1–8*), commercial silicone antifoams appear to be the most generally suitable since they are active at low concentrations and act on most types of foams.

Mechanical antifoaming techniques have the advantage that no chemical contaminants are introduced. Suggested methods include centrifugation (*4*), tangential air blasts (*4*), heat (*4, 9*), and narrow constrictions (*10*).

Elimination of foaming by headspace purge techniques (*11*) or foam traps (*12, 13*) has also been suggested. These can be useful antifoaming techniques, but they depart significantly from the usual purge and trap in that gas is no longer bubbled through the sample and system dynamics are significantly altered.

Silicone antifoaming agents have been found effective in purge and trap analysis (*9, 13*), although in one report gradual decreases in sensitivity and carrier gas flow were observed (*13*). By use of a mass spectrometer as the gas chromatographic (GC) detector, significant persistent contaminants were observed with the use of a silicone antifoam (*9*).

The object of this research was to develop a protocol for the handling of samples which foam during purge and trap analysis. Foam can climb through the apparatus, enter the trap and invalidate the analytical data by irreversibly contaminating the trap. The protocol developed had to be simple, reproducible, accurate, and congruent with the Bellar and Lichtenberg (*14–17*) technique currently used for priority pollutant analyses. Addition of chemical antifoaming agents and modification of glassware were considered potentially useful techniques. The goal was to develop a procedure (a) requiring minimal attention by the analyst, (b) utilizing a minimally modified apparatus, (c) providing efficient recovery of priority pollutants, and (d) adding no new artifacts to the analysis.

EXPERIMENTAL SECTION

Model Compounds. Test compounds were chloroform, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, 1,1,2-trichloroethane, bromoform, 1,1,2,2-tetrachloroethane, toluene, and chlorobenzene.

A stock solution in methanol was used to fortify water and wastewater samples. Aqueous stock solutions were prepared fresh daily by addition of 1 μL of the methanol standard to 100 mL water or foaming solution.

Standard Foaming Solution. The standard foaming solution contained 3 g/L NH_4Cl, 1 g/L K_2HPO_4, 0.25 g/L $MgSO_4 \cdot 7H_2O$, and 0.25 g/L KCl in distilled water which had been purged under nitrogen for 16 h at a pH of 7.1 to simulate the mineral content in an environmental sample. The antifoaming abilities of several antifoams were tested on the surfactant sodium dodecyl sulfate (50 mg/L) and confirmed by using dodecylbenzenesulfonate (50 mg/L) or egg albumin (100 mg/L).

Foaming Test. The method found most reliable was the passage of a known volume of gas through the test solution followed by measurement of the volume of foam. Nitrogen (~100 mL) was bubbled through 25 mL of the test solution containing the test antifoam in a 44 × 2.5 cm i.d. fritted glass chromatography column. The foam height was measured immediately after stopping the N_2 flow. The value reported was the ratio of the volume of foam to volume of gas introduced (V_{foam}/V_{N_2}). Several other test methods, including equilibrium foam height and foam half-life, were investigated and found inadequate.

Analysis. The purge and trap system was patterned after the system developed by Bellar and Lichtenberg (*11, 13–17*). Samples were analyzed on a Fisher-Victoreen 4400 gas chromatograph with a flame ionization detector (FID) and a Tracor Model 700 Hall electrolytic conductivity detector operated in the halide mode. The split ratio between the two detectors was approximately 1:1. The chromatography column was a 2 mm i.d. × 180 cm glass column packed with 0.2% Carbowax 1500 on 60/80 mesh Carbopack C. The column temperature was held at 60 °C for 4 min and then programmed at 6 °C/min to a final temperature of 180 °C. Samples were purged onto the Tenax sorbent trap for 12 min

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Table I. Foam/Nitrogen Ratio for Candidate Antifoams (SDS Solution)[a]

	V_{foam}/V_{N_2}			
antifoaming agents	10 ppm	50 ppm	100 ppm	1000 ppm
blank	1.06–1.12			
DC C	0.19	0		
DC FG-10	1.13	0		
DC DB 31	0.19	0		
DC DB 110A	0.74	0		
DC A	0.94	0.19		
DC 544	0.83	0		
GE AF-60	0.72	0		
GE AF-72	0.69	0		
GE AF-75	1.02	0.17		
GE AF-93	1.04	0.32		
Witco balab 140	1.08	1.07		
Witco balab 260	1.07	0.92		
Witco balab 748	1.09	0.92		
Witco balab 3056A	1.09	0.9		
Surfynol 440[b]	1.04	1.11		
Surfynol-PC[b]	1.07	1.09		
Surfynol-104[b]	1.08	1.16		
lauryl alcohol			1.25	1.33
propylene glycol		1.05		1.1
polypropylene glycol (Carbowax 600)			1.27	1.31
methyl *n*-docosanoate			0.14	0.77
methyl *cis*-13-docosenoate	1.15		0.89	
methyl *cis*-15-tetracosenoate	0.97		0.50	
methyl *n*-hexanoate			1.23	1.17
1,6-hexanediamine		1.06		1.10

[a] Standard foaming solution containing sodium dodecyl sulfate at 50 mg/L. [b] Based on 2,4,7,9-tetramethyl-5-decyn-4,7-diol; from Air Products Corp.

with a nitrogen flow of 40 mL/min. The trap was then heated from ambient temperature to 180 °C in ~50 s and maintained there for 4 min while trapped materials were back-flushed with nitrogen onto the GC column. Between analyses, the purge flask was washed twice with distilled water and then dried with nitrogen at ~150 mL/min.

To help minimize recovery problems and to aid in cleaning the purge flask between samples, a three-way syringe valve (Becton-Dickinson) was attached to the sample loading syringe and the third port connected to an aspirator. This allowed continuous back-flushing of the heated trap following thermal desorption. A carbon trap was placed at the desorption/injection system vent to remove organics from the laboratory air, which were being drawn through the trap. It was found that 4–6 min of continuous back-flushing were sufficient to clean the trap in most cases and also allowed sufficient time for the trap to cool for the next sample.

Further validation was conducted by using purge and trap/gas chromatography/mass spectrometry/computer. The purge and trap system was interfaced with an LKB 2091 magnetic sector mass spectrometer (MS). The GC was operated as described above, except the carrier gas flow rate was 18 mL/min, the limit of the separation and pumping system.

RESULTS AND DISCUSSION

Evaluation of Chemical Antifoams. Chemical compounds and commerical antifoaming agents were evaluated for antifoaming ability and purity. The candidate antifoams were selected from commerical manufacturing literature and based upon a review of the scientific literature (*1–8*). The antifoams were evaluated at two or three concentrations in an attempt to assure that an effective amount of antifoam was present. The results given in Table I indicate a wide range of antifoaming performance for a sodium dodecyl sulfate (SDS) solution. On the basis of these results, the six best antifoams were chosen. Further evaluation of these six antifoams was conducted by using another standard detergent foaming solution of sodium dodecylbenzenesulfonate (SDBS) at a concentration of 50 mg/L and a protein foaming solution (100 mg/L egg albumin). The results are listed in Table II. Dow Corning (DC) Antifoams C and DB 31 and General Electric (GE) AF 60 and AF 72 were the four most effective antifoaming agents in these tests.

Table II. Foam/Nitrogen Ratio for Selected Antifoams (SDBS and Albumin Solutions)[a]

	SDBS solution		egg albumin	
antifoam	10 ppm	50 ppm	10 ppm	50 ppm
blank	1.08		0.45, 0.24	
DC C	0.93	0.06	0.05	0
DC DB 31	0.61	0	0.05	0
DC 544	1.05	0.16	0.06	0.02
DC DB 110A	1.02	0.24	0.06	0.03
GE AF 60	1.02	0.04	0.03	0
GE AF 72	1.07	0.41	0.03	0

[a] Standard foaming solution containing sodium dodecylbenzenesulfonate (50 mg/L) or egg albumin (100 mg/L). Foaminess measurement: volume of foam/volume of nitrogen bubbled through the standard foaming solution in a 2.5 cm i.d. column with a glass frit at the bottom.

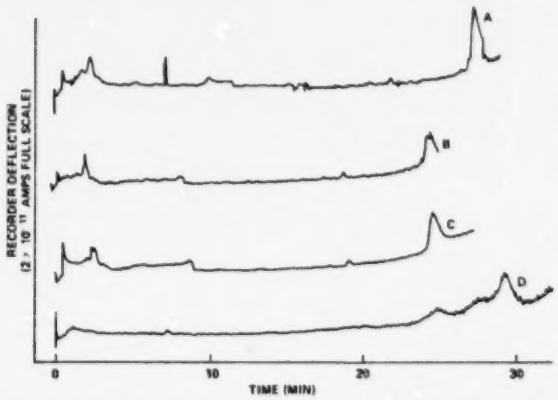

Figure 1. Analysis of purified antifoaming agents as monitored by purge and trap/GC/FID: (A) ~1 mg General Electric AF72 in 5 mL of distilled/purged water; (B) ~1 mg Dow Corning Antifoam C in 5 mL of distilled/purged water; (C) distilled/purged water; and (D) trap blank.

The purity of the antifoams was assessed by comparison of the purge and trap/GC/FID chromatograms of the antifoam at 100 ppm vs. distilled water. On the basis of these chromatograms, it was determined that the antifoams must be further purified for use in purge and trap analysis. The antifoams were purified either in vacuo at 120 °C for 48 h or under a stream of dry nitrogen at 50 °C for 4 h. The Dow Corning antifoams became waxy solids which did not easily reemulsify with water. The General Electric antifoams separated into an oil and a siliceous precipitate. When reemulsified by shaking with water, the GE antifoams swelled into globules which floated in the water. In spite of these problems, the antifoaming properties of all four antifoams were retained after purification and "resuspension" in water. Figure 1 shows the comparison of chromatograms representing a trap blank, a purge of distilled water, and purges of two antifoams. The antifoams contributed no observable interferences to the analysis. Purity was also checked by purge and trap/GC/MS to assure that compounds insensitive to FID were not present. No interferences were observed with the mass spectrometer as detector.

Table III. Recoveries (%) of Volatile Organics from Distilled Water Standards with Selected Antifoams[a]

compound	antifoams			
	DC-C	DC-DB31	GE AF72	GE AF60
chloroform	96 ± 0.3	121 ± 28	104 ± 2	100 ± 0.7
1,1,1-trichloroethane	96 ± 1	78 ± 5	90 ± 2	95 ± 0.2
carbon tetrachloride	100 ± 2	94 ± 31	87 ± 4	88 ± 1
bromodichloromethane	111 ± 20	87 ± 3	103 ± 2	103 ± 1
trichloroethylene	93 ± 0.2	98 ± 0.6	91 ± 2	92 ± 0.4
1,1,2-trichloroethane	97 ± 0.3	93 ± 3	101 ± 1	108 ± 0.3
bromoform	100 ± 0.3	93 ± 7	95 ± 1	98 ± 0.5
1,1,2,2-tetrachloroethane	98 ± 0.2	80 ± 3	103 ± 1	105 ± 0.5
toluene	91 ± 1	96 ± 6	93 ± 5	115 ± 0.2
chlorobenzene	94 ± 0.5	98 ± 0.5	97 ± 0.4	91 ± 0.3
mean	98 ± 5	94 ± 12	96 ± 6	99 ± 8

[a] 100 ppm antifoam added; recoveries measured against purge from spiked distilled water; triplicate determinations.

Three methods of antifoam addition were investigated to determine which most effectively dispersed the antifoam in the water sample. The most reliable and convenient technique was the addition of the purified antifoam directly to the water sample in the purge flask. The other techniques tried, coating the inside of the purge flask with antifoam prior to sample introduction and mixing antifoam with the water sample prior to transfer to the purge vessel, were judged either less effective or more cumbersome.

Effect of Antifoaming Agents on Purge and Trap Recoveries. Recovery studies using both distilled water and the foaming solution indicated that the antifoaming agents did not significantly alter the recovery of model priority pollutants. The data are discussed below.

Recoveries of model compounds, which represent the range of volatilities and polarities normally determined by purge and trap, from distilled water with and without four antifoaming agents were compared. The antifoams were spiked into the water standard at 100 ppm, the mixture was shaken to disperse the antifoam, and an aliquot was transferred to the purge vessel using a syringe. The results shown in Table III indicate that the antifoaming agents do not significantly affect purge efficiency.

The effect of antifoaming agents on the purgeability of volatile organics from both water with antifoam and the foaming solution with antifoam was also studied. On the basis of the results listed in Table IV, it appears that neither the antifoam nor the synthetic foaming solution has a measurable effect on the recoveries of the compounds studied.

Evaluation of Physical Antifoaming Devices. Several modifications to the Bellar and Lichtenberg purge apparatus were tested for effectiveness in arresting foams during the analysis of water samples. Two of the modifications trapped the foam in large reservoirs (*12*, *13*), resulting in a partial headspace purge of the sample. These were both reasonably efficient purge techniques but were plagued by memory problems and unwieldly glassware. The third technique, breaking the foam with heat (*9*), generated an aerosol which quickly contaminated the trap and other portions of the analytical system.

Evaluation of Combined Physical and Chemical Techniques. The chemical antifoams controlled the foam well in most situations; however, the antifoam was occasionally overwhelmed and some foam would escape the purge flask. It has been noticed that any foam produced in the presence of the chemical antifoam was very short-lived. Thus, if given time to break up, external foam traps would be unnecessary. On the basis of this hypothesis, two techniques were investigated: slower purge rates and a larger purge vessel.

Related research has shown that recovery efficiency is independent of flow rate but is dependent on total purge gas volume (*18*). Therefore purges could be effected by slowing the purge rate with corresponding increases in purge times. With careful regulation of the flow rate through the purge vessel in conjunction with a chemical antifoam, foaming could be controlled. At slow gas flow rates, the foam is given more time to break up. This technique, although effective, required constant operator attention and was, therefore, judged inadequate.

Table IV. Effect of an Antifoaming Agent and the Standard Foaming Solution on Purge and Trap Efficiency for Selected Priority Pollutants

compound	water recovery (% ± SD)[a]	foaming solution
chloroform	157 ± 28	118
1,1,1-trichloroethane	78 ± 5	78 ± 22
carbon tetrachloride	100 ± 31	133
bromodichloromethane	87 ± 3	87 ± 16
trichloroethylene	100 ± 0.5	91
1,1,2-trichloroethane	93 ± 3	91 ± 14
bromoform	87 ± 7	140
1,1,2,2-tetrachloroethane	80 ± 3	83 ± 14
toluene	96 ± 6	97 ± 23
chlorobenzene	101 ± 0.4	100
mean	98 ± 22	102

[a] Recovery based on a ratio of the amount purged from either the water with antifoam or the standard foaming solution with antifoam vs. spiked distilled water (defined as 100%). The data indicate the effect of the antifoaming agent (DC-DB-31) and of the synthetic foaming solution on the recoveries. Triplicate determinations if standard deviation is listed, otherwise single determination. All compounds spiked at about 200 μg/L.

With a larger purge vessel (~60 mL capacity) in conjunction with a chemical antifoam, the foam was given adequate time and space to disperse and fall back into the sample. After experimenting with different sized purge flasks, we selected the apparatus shown in Figure 2. The indentations help collapse the foam and the tall, narrow configuration eliminates any unswept headspace which could decrease recovery efficiency. This technique was the best of all techniques tested, permitting analysis of foaming samples with no operator attention and without unwieldy apparatus.

Selection of a Recommended Protocol. All four of the top candidate antifoams (Dow Corning DB-31 and Antifoam C and General Electric AF60 and AF72) were found to be suitable. However, problems with redispersion of the Dow Corning antifoams and slightly lower purity of the AF60 made the General Electric AF72 the antifoam of choice. All validation studies were done by using this antifoam.

On the basis of the results discussed above, neither a chemical antifoam nor a physical antifoaming device by itself is sufficient for all samples. The combination of a silicone antifoam and the large purge flask proved the most effective

Table V. Compounds Found in Paint Manufacturing Wastewater Sample (P1-M2-T)

chromatographic peak no.	compound
1	CO_2
2	acetaldehyde
3	ethanol and unknown
3a	acetone
3b	methylene chloride
4	propanol
5	unknown
6	butanol (tent.)
7	methyl ethyl ketone
8	unknown
9	unknown
10	unknown
11	unknown
12	unknown
13	cyclopentanone
14	4-methyl-2-pentanone
15	2-hexanone
16	siloxane compound (bkg)
17	unknown
18	unknown
19	3-heptanone
20	2-heptanone
21	siloxane compound (bkg)

Table VI. Reproducibility of Purge and Trap Standards

compound	RSD of peak heights[a]
1,1,1-trichloroethane	6.7
carbon tetrachloride	11
bromodichloromethane	2.3
trichloroethylene	5.0
1,1,2-trichloroethane	4.7
bromoform	4.3
1,1,2,2-tetrachloroethane	4.0
chlorobenzene	5.0
mean	5.4

[a] Percent relative standard deviation of normalized peak heights (peak height × attenuation) for five injections at each of three concentrations.

technique tried and was selected for the final validation.

The procedure ultimately developed is as follows: Two drops of purified commerical antifoam (General Electric AF72 or Dow Corning Antifoam C) were added to 5.0 mL of sample contained in the 60-mL volume purge flask and purged according to the routine purge and trap protocol (*12*).

Validation. The technique was qualitatively validated by analysis of several samples using purge and trap/GC/MS. Two samples of paint manufacturing effluent, an oil refinery biopond feed, and a detergent manufacturing scrubber water were analyzed. A total of 11 analyses, including blanks were performed. The chromatogram from one of the paint manufacturing samples is shown in Figure 3 and the list of compounds identified is found in Table V. The siloxane compounds, peaks 16 and 21, are often encountered on this system without the purge and trap and are probably not resultant from the antifoam. The purge and trap/GC/MS system performed the 11 analyses over about 10 h with no malfunctions or problems due to the antifoam. No contamination was observed on subsequent chromatographic runs. The only problem observed was that five of the analyses were interrupted when the pressure in the mass spectrometer forced temporary shutdown to protect the source. This high pressure was apparently caused by water vapor desorbed from the Tenax/silica gel trap.

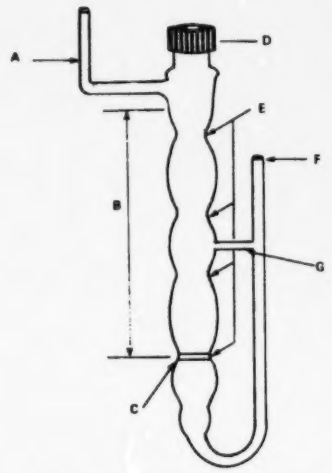

Figure 2. Purge flask for foaming samples. Internal volume is about 60 mL; designed for a 5-mL wastewater sample: (A) $^1/_4$ in. o.d. exit; (B) 26 cm × 2.0 cm o.d.; (C) 15 mm medium-porosity glass frit; (D) screw cap septum to fit 14 mm threads; (E) ~1.5 cm o.d.; (F) $^1/_4$ in. o.d. inlet; (G) glass support brace.

The reproducibility of the technique was investigated by replicate analyses of the standards in distilled water. the concentrations used ranged from 2 to 32 μg/L and the reproducibility data are listed in Table VI. An overall precision of ±5% was established.

Four different wastewaters were used to validate the technique: a municipal sewage sample, a paint manufacturing wastewater, a detergent manufacturing wastewater, and a chick hatchery wastewater. The paint manufacturing wastewater had a mean foam ratio (V_{foam}/V_{N_2}) of 1.26, the detergent manufacturing wastewater, 1.40, and the sewage

Table VII. Recoveries of Model Compounds from Wastewater Samples[a]

compound[b]	mass spiked, ng/mL	chicken hatchery recovery (%)[c]	chicken hatchery RSD[d]	paint manufacturer recovery (%)	paint manufacturer RSD	municipal sewage recovery (%)	municipal sewage RSD	detergent manufacturer recovery (%)	detergent manufacturer RSD
1,1,1-trichloroethane	67	100	7	124	18	91	4	84	12
carbon tetrachloride	159	206	9	133	18	135	7	123	9
bromodichloromethane	99	112	4	99	10	108	8	74	5
trichloroethylene	73	127	4	99	10	114	9	107	9
1,1,2-trichloroethane	29	100	3	90	11	103	7	76	4
bromoform	145	85	7	55	9	84	17	89	3
1,1,2,2-tetrachloroethane	32	63	6	78	17	91	7	63	5
chlorobenzene	11	ND[e]		ND[e]		ND[e]		109	8
mean		113	41	84	54	104	16	88	24

[a] Corrected for mean background (five replicates) in unspiked wastewaters. [b] Compounds added to wastewaters at level specified. [c] Mean of five replicates. [d] Relative standard deviation (RSD). [e] Not detected, interference.

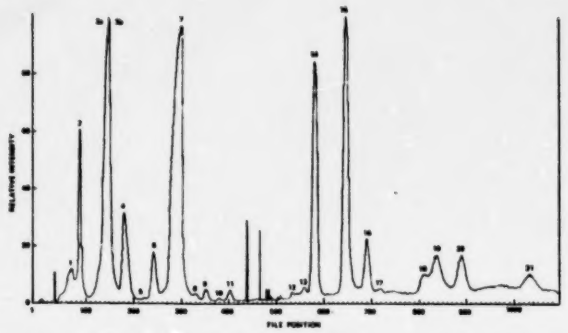

Figure 3. Total ion current chromatogram of purge and trap/GC/MS analysis of a paint manufacturing wastewater sample. See Table V for peak identifications.

effluent, 0. Five replicate aliquots of each wastewater were analyzed, followed by five aliquots fortified with the compounds under study. Recoveries were measured against a standard curve prepared from purges of standard solutions at three concentrations performed throughout each day. Of the four wastewaters validated, the detergent manufacturing wastewater produced the most foam. With this wastewater, thick white foam developed which reached a height of 18–22 cm in less than 1 min. At that point, the foam began to break up, eventually reaching an equilibrium height of 5–8 cm, where it remained for the duration of the purge.

Recoveries from the wastewater samples are listed in Table VII. The average overall recovery from the four wastewaters was 97%, indicating that neither the antifoam nor the wastewater matrices interfere significantly with the recovery of spiked purgeable organics. The decreased precision of these results relative to distilled water, however, can be attributed to the complex matrices.

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